

(19) European Patent Office

[bar code]

(12) European Patent Announcement

(11) EP 1 031 375 A2

(43) Publication Date:

(51) Int. Cl.: B01J 19/00

30 August 2000 / Patent Folio 2000/35

(21) Announcement No. 00103012.1

(22) Announcement Date: 15 February 2000

(84) Stipulated Agreement States

AT BE CH CY DE DK ES FI FR GB GR  
IE IT LI LU MC NL PT SE

Stipulated Extension States

AL LT LV MK RO SI

(30) Priority: 24.02.1999 DE 29903296 U

(72) Inventors:

Oberbeck, Sebastian  
65753 Greifenstein, Germany

Schwalbe, Thomas Dr.  
61118 Bad Vilbel, Germany

(74) Representative: Benz, Jürgen, Dr.

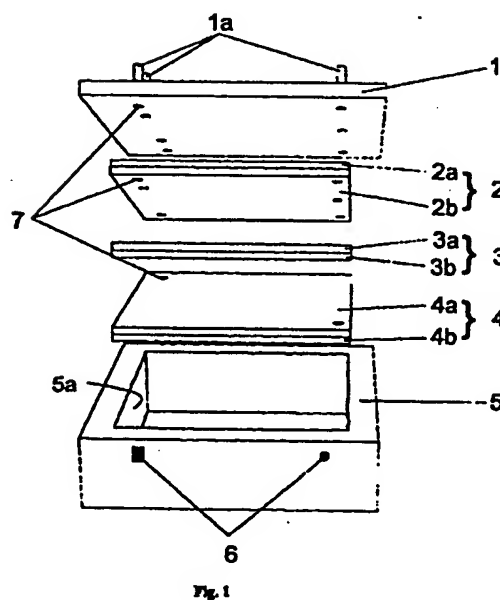
Kanzlei Heumann, Benz  
Spessarting 63  
64287 Darmstadt, Germany

(71) Reporter:

CPC Cellular Process Chemistry GmbH  
60343 Frankfurt, Germany

#### (54) Microreactor

(57) The invention concerns a microreactor for conducting chemical reactions whereby the conduct of the chemical process takes place in horizontal spaces that are formed by two or more superimposed plates or laminae, characterized by the fact that these plates or laminae have sealed zones that produce a fluid-tight and gas-tight union between the individual function modules and to the outside; and the fact that the plates or laminae are arranged in a device in such a manner that the sealed zones of the plates or laminae can be pressed into each other in a sealing manner.



[0001] The invention concerns a microreactor for conducting chemical reactions, whereby the conduct of the chemical process takes place in horizontal spaces that are formed by two or more plates or laminae stacked one above the other, whereby these plates or laminae have integrated sealed zones that produce a fluid-tight and gas-tight union between any two layers adjacent and to the outside; and whereby the plates or laminae are arranged in a device with a suitable size in such a manner that the sealed zones of the plates or laminae can be pressed into each other in a sealing manner.

Such a microreactor represents a miniaturized reaction system for industrial processing and chemical processing technology. A microreactor of this conceptual type is known for example from EP 0 688 242 B1. This microreactor is made of many stacked small plates that are connected with each other, upon the surfaces of which there are micromechanically produced structures that form reaction spaces in their reciprocal effect, in order to conduct the desired chemical reactions. There is at least one channel leading through the system, which has an inlet and outlet connection. The individual small plates are rigidly bonded together so that the microreactor, once built, cannot be modified to match altered conditions. According to the instruction contained in this document, special microreactors must be constructed for specific types of reactions. A given microreactor can be used for only a few uniform operations.

In DE 196 52 823 a microreactor system is proposed that can be assembled and disassembled again without damage, in which the individual layers are fixed and sealed using polytetrafluorethylene spacers. The disadvantages of this system are based on the fact that the individual layers and spacers must be positioned very carefully and that the spacer materials are not inert against all reaction conditions introduced in the course of the chemical synthesis. In addition, the spacers that are introduced can lead to problems with respect to the permeability of the individual channels and to increased production costs.

[0002] The invention meets the goal of making a microreactor system that makes it possible to

achieve a simple modification of the microreactor system to accommodate different process conditions, while avoiding the disadvantages of known systems. The microreactor should maintain an exact temperature control of the reaction process and, as desired, produce targeted laminar or turbulent flow in different areas. The microreactor also should be economical to manufacture in order to be used if needed in a single-way system. The different function modules (heat exchanger, mixer = reactor, dwell paths, condensers, distillation and / or extraction vessel) can be manufactured in a standardized manner independent of the given reaction type that is to be conducted. By selecting the liquid feed openings these standard function modules can be combined as needed, and permanently or temporarily connected to each other.

It should also be possible to achieve the setup of various arrangements, geometries, and sizes of the reactor.

[0003] The goal is met based on the characteristics of claim 1 and is given form and further substance by the other characteristics of the subordinate claims. To give details, functional modules are formed that can be suitably assembled together with respect to the chemical process reaction to be conducted, and they can be connected with each other. The modular construction approach makes it possible to achieve a simple modification to the given changing conditions as they occur, in that individual elements of the microreactor can be switched in and out, in order to satisfy the requirements of the reaction that has been selected, or when the expected results do not occur, or when there are breakdowns.

[0004] By exchanging the components of the microreactor of this invention, the feed of liquid can finally be dimensioned in such a manner that an improved temperature control of the reaction is established, or so that a higher selectivity and a decrease in observed undesirable reaction by-products is observed, i.e., one obtains reaction products that contain less impurities.

The dimensions and form of the microreactor according to this invention are not critical in themselves. By definition, in a microreactor the

size of at least one component is less than 1 mm.

[0005] The individual plates or laminae can be present in any geometric shape. Preferably they should be round, oval, square, or rectangular. Square plates are especially preferred with regard to their positioning capabilities.

[0006] Of essential significance for proper functioning of the microreactor is fluid-tight and gas-tight connection between the individual modules of the microreactor. For this purpose, the surface areas of the plates are specially treated, the fluid channels are appropriately drawn, and the connections are engineered so that during assembly of the modules sufficient security from leakages is guaranteed. The integrated sealing zones are preferably formed in such a manner that they have an extremely smooth surface. Especially preferred are sealing zones whose roughness is less than 1  $\mu\text{m}$ . In another preferred application form, the sealing zones are made so that a raised, preferably sharp edge of one plate grips into the smooth surface of a second plate.

[0007] While the methodological individual operations are given in the individual operation modules, these are connected with each other by vertical channels in order to treat the fluid further from level to level. The function modules themselves contain horizontal channels and spaces that are cut for the given process step that the module is designed for. Between the channels and the spaces there are separation barriers that become sealed based on the pressure exerted on the stack in the function module. Thus it must be established that vertical channels are available for the input and output of reactants and auxiliary media while the reactions themselves occur in the spaces that extend horizontally.

[0008] The stack of function modules is contained by a device, preferably enclosed by a housing, which also holds the fluid connections for the media to be reacted as well as output of the desired product. This device itself is preferably formed as a tension device, or special tension devices take care of ensuring that sufficient surface pressure is applied between the individual function modules in order to guarantee their sealing. The device has

connection stubs that are pressed into the arranged openings in the vertical channels of the function modules, whereby the contact surfaces between the connection stubs and the openings are preferably conical or spherical in shape, without having to be cylindrical in shape. For regulating the pressure, spring loaded pressure plates can be used. Pressurized air cushions or something similar also can be used for the same purpose in the lower portion of the device. Furthermore, pressure can be exerted on the individual plates or laminae based on thermal expansion, magnetic, piezoelectric, hydraulic, pneumatic, or electrostatic attraction or repulsion, or based on a shape memory effect.

[0009] Materials that may be considered for the plates or laminae include metals (stainless steel), glass, ceramic, semiconductor material, particularly that based on silica, as well as synthetic materials. The selection of these work materials or combinations of same is controlled by the application that is provided. Stainless steel is especially preferred.

[0010] During the conduct of the chemical process, various parameters must be observed. Therefore the insertion of sensors into the microreactor is provided for, in particular sensors for capturing the temperature, pressure, and in some cases the flow rate and volume flow. The housing has appropriate leads for these sensors, and when possible, these sensors are attached outside the microreactor system. However, in part having sensors in the function modules is unavoidable. The sensors are connected with control circuits in order to be able to control and manage the course of the reaction. The appropriate logic circuit can be installed on the housing or be located outside the housing.

[0011] The invention is described based on the drawings. Of these Figure 1 shows a microreactor in schematic, exploded representation, and Figure 2 shows a magnification of details of the microreactor.

[0012] Between the housing cover 1 and a housing 5, a number of functional modules 2, 3, and 4 are arranged, all of which are held by the assembly under pressure, to compress the sealing surfaces between the modules. Each

function module 2, 3, and 4 contains a module half 2a, 2b, or 3a, 3b, or 4a, 4b, which is shaped like a frame in order to provide sealing surfaces 10 that seal upon pressing the halves together. In the cover, there is a fluid connection 1a installed, which proceeds in fluid channel 7 through the boundary areas of the function module. From there, there are horizontal channels to reaction spaces 8, which as a rule contain a channel system or labyrinth system. The reaction channels of reaction spaces 8 run in general diagonally or crisscross each other.

[0013] The function modules built of two halves have at their surface always an opening for the channels 7, which are arranged in standard spacings, in order during the buildup of the stack to flood precisely 10 of function modules to each other. These openings are provided with sealing structures in order to couple the running channel 7 in a sealing manner. These sealing coupling extensions can be shaped as a cylindrical stubs with conical or spherical shaped sealing surfaces and can be sufficiently pliable so that the plate-formed function modules lie one on the other with their entire boundary area in order to transfer the force of the pressure onto the inner lying sealing surfaces 10.

[0014] In the application example shown it is assumed that the function module 2 represents a heat exchanger that is composed of a heat exchanger half 2a for a cooling or heating agent, and a heat exchanger half 2b for feeding reactant. Function module 3 would be a mixer composed of a mixer half 3a for feeding a reaction partner A and a mixer half 3b for feeding a reaction partner B. Function module 4 represents a dwell path that is composed of a dwell path 4a for reaction product and a dwell path 4b for a cooling or heating medium.

[0015] Housing 5 has a housing space 5a, the size of which is adapted to receive function modules 2, 3, and 4. Underneath in housing 5 there can be yet a spring pressure layer, which is not shown and which consists of springs with pressure plate. Alternatively, a simple pressure pillow can be used, with which the necessary pressure can be produced between the sealing surfaces 10.

[0016] As installed, the cover 1 is rigidly fastened on the housing 5; for this purpose one can use screws or clamps if one is dealing with a soluble mixture. One can also use welding, bonding, gluing, soldering, or riveting techniques if the housing cover 1, housing 5, and / or function modules 2, 3, and 4 are to be used only one time. Housing 5 can also include pass-throughs for sensors 6 in order to control certain parameters of the chemical reactions occurring in the reactors. Such sensors would include primarily sensors for temperature, pressure, flow rate, volume flow or mass flow, as well as pH value.

[0017] Another object of the inventions in a process for the production of a microreactor, in accordance with this invention, for conducting chemical reactions, which include the following steps:

- (a) Production of many plates or laminae, the surface of which are micro-technically or precision technically structured so that they have sealing zones and — together with the surface of other plates or laminae — horizontal reaction spaces
- (b) Stacking of the individual plates or laminae in an appropriate sequence and orientation into a suitable housing
- (c) Contact pressure of the housing cover so that the sealing zones of the individual plates or laminae are pressed against each other to seal them.

[0018] The structuring in step (a) can be the result of etching, cutting and drilling by laser and water jet methods, punching and stamping, machining, planning and drilling, injection molding and fusing, as well as by spark erosion and in combination of these methods.

[0019] Preferably the metal sheets of the individual plates or laminae are produced by etching or laser cutting and / or drilling. In this case the outer contours and the drill holes are produced preferably by laser cutting or drilling and the channel structures are produced preferably by etching. Starting with a drawing, during etching first a mask is produced that contains the positive or negative representation

of the geometry. Then a light-sensitive lacquer is spread on the substrate, preferably a metal sheet, on which as a rule there is a layer of polymethylmethacrylate (PMMA) that is a few  $\mu\text{m}$  thick, which is illuminated with the help of the mask and ultraviolet light. In the areas that are illuminated or not illuminated (each according to the positive or negative resist) the lacquer is removed with an organic solvent, preferably acetone. The substrate that is lacquered, illuminated, and developed in this manner is dipped into an appropriate etching solution in which the exposed surface is subjected to the etching attack for as long as is necessary until the desired etching depth is achieved.

[0020] The layers must be stacked one on the other in such a manner that the fluid feeds and separation walls are maintained completely, and that a complete fluid-tight and gas-tight union between the individual layers results.

[0021] If the surface roughness lies in the area of 1  $\mu\text{m}$  or less and the surface is absolutely free of scratches, is clean, and is free of grease, then it is possible to achieve a gas-tight superimposition of sheets by applying an even, mechanical pressure on the stack. Essential for this is that the remaining gap is less than 1  $\mu\text{m}$ . This creates such a strong flow resistance between the plates that fluids can enter slightly into the gap but do not produce any leaks, since no flow can arise as it does for example in capillaries.

[0022] The material from which the function modules are made must necessarily depend primarily on the materials to be handled and the chemical processes. In general, work materials that are appropriate for chemistry include stainless steel, glass, ceramic, synthetic material and semiconductor materials, as well as combinations of these materials. The same also holds for the housing and the housing cover.

[0023] In order to be able to adapt to changing conditions, there are also various sized housings with housing covers, in order to be able to accommodate various numbers of function modules. This selection from possible components makes it possible, if necessary, also to switch out individual components if their

function is found to be less than optimal, or if a problem should occur.

[0024] Another object of the invention is therefore a construction assembly for production of a microreactor, in accordance with the invention, for conducting chemical reactions, which consists of the following construction components:

- (a) an assembly of several plates or laminae, the surfaces of which have integrated sealing zones, and — together with the surface of other plates or laminae — horizontal reaction spaces
- (b) one or more devices into which the individual plates or laminae can be fit precisely and can be stacked in various, appropriate series, and
- (c) devices for applying pressure on the plates or laminae so that the sealing zones of the individual plates or laminae can be pressed against each other in a sealing manner.

[0025] Based on such a construction assembly, the user is in a position to modify the microreactor as appropriate to his needs. Extremely exothermic reactions, for example, can be better managed using several heat exchange modules arranged in sequence. In contrast, slow reactions, for example, can be better optimized by installing several function modules with dwell zones and / or heating zones.

[0026] Altogether, the invention represents a modularly constructed, miniaturized reaction system that makes it possible to integrate various functions that are important for the control of the process. These functions are understood to include the feed of reactants, their pre-processing heat treatment, the admixture of reactants under controlled thermal conditions, an internal thermal treatment as well as post-processing dwell period and the removal of the reaction product to suitable container vessels.

[0027] Furthermore, the object of the invention is also a method for conducting chemical reactions whereby one or more chemical reactants in gas form and / or fluid form are

mixed and brought to reaction in of two or more plates or laminae that are stacked over each other in horizontal areas of a microreactor that is built in accordance with the invention.

[0028] The concept "fluid form" includes both reactants that are present themselves in an aggregate fluid state and reactants that are introduced in a mixture with a fluid diluent. In one application that is especially preferred, at least two reactants are brought into reaction with at least one diluent in a microreactor in accordance with this invention. Preferred diluents are halogenated aliphatic or aromatic hydrocarbons such as, for example, hexane, cyclohexane, dichlormethane, tetrachlormethane, benzol, toluol or chlorbenzol; also ethers such as, for example, diethylether, *tert*-butylmethylether, dioxane, or tetrahydrofurane; ketones or amides such as, for example, acetone, methylethylketone, dimethylformamide, or N-methylpyrrolidone; or alcohols such as, for example, methanol, ethanol, propanol, isopropanol, or butanol; or acetonitrile, or water, or mixtures of these diluents.

[0029] To make it easier to understand this invention, the following illustrative examples for possible reaction types are presented. This invention is not restricted to these specific application examples, but rather includes the full extent of the patent claims.

[0030] Examples of reactions in accordance with this invention are conversions of electrophilic reactants with nucleophilic reactants, such as for example the reaction of an amine with a carbonic acid chloride with the formation of a carbonic acid amide; or conversion of a diene with a dienophil with formation of a cyclohexane.

#### Patent Claims

1. Microreactor for the conduct of chemical reactions, whereby the conduct of the chemical process occurs in horizontal spaces that are formed by two or more plates or laminae stacked over each other, characterized by the fact that these plates or laminae have integrated sealing zones, which produce a fluid-tight and gas-tight

connection between any two superimposed layers and also to the outside; and that the plates or laminae are arranged in a device with suitable size so that the sealing zones of the plates or laminae can be pressed against each other in a sealing manner.

2. Microreactor in accordance with claim 1, whereby the plates or laminae (2a, 2b, 3a, 3b, 4a, 4b) are stacked over each other in such a manner that channels and spaces that extend horizontally (8) are formed for conducting the chemical process, whereby function modules (2, 3, 4), are formed in which individual physical or chemical processes can be conducted, characterized by the fact that
  - (a) the function modules contain sealing zones (10) in order to produce a fluid-tight and gas-tight connection between the individual function modules and toward the outside, and different function modules (2, 3, 4) can be selected and assembled based on the desired reaction systems
  - (b) a housing assembly (1, 5) that has a suitable housing size in order to accept the reaction system and press the sealing zones (10) of the function modules together in a sealing manner.
3. Microreactor in accordance with claim 1 or 2, characterized by the fact that the conduct of the process includes the followings steps:
  - feed of reactants
  - their pre-processing heat treatment
  - admixture of the reactants under controlled thermal conditions
  - an intermediate thermal treatment
  - a post-processing dwell time
  - removal of the one or more reaction products
4. Microreactor in accordance with claims 1 through 3, characterized by the fact that the function modules are provided with previously prepared vertical channels (7) for connection with neighboring function modules.

5. Microreactor in accordance with claim 4, characterized by the fact that the sealing-contact surfaces include interlocking conical, spherical, or cylindrical shapes.

6. Microreactor in accordance with claims 1 through 5, characterized by the fact that springs are provided for installation in the housing (1, 5) in order to maintain a predetermined compression between the function modules.

7. Microreactor in accordance with claims 1 through 6, characterized by the fact that each housing (1, 5) includes a cover (1) and a housing bottom portion (5) that can be connected with each other by screws or clamps.

8. Microreactor in accordance with claims 1 through 7, characterized by the fact that the housing (1, 5) has pass-throughs for electrical connections as well as sockets on its outside for attendant electrical connections and / or signal leads from sensors (6), which are installed either in the housing wall or in the individual function modules for controlling process parameters such as temperature, pressure, flow rate, volume or mass flow, pH value.

9. Microreactor in accordance with claim 8, characterized by the fact that control paths are provided, which based on the measured parameters control the material flow in the fluid connections as well as the energy input and output with respect to the function modules.

10. Microreactor in accordance with claims 1 through 9, characterized by the fact that the function modules (2, 3, 4) consist of two plates or laminae (2a, 2b; 3a, 3b; 4a, 4b), on the surface of which horizontal channels and reactions spaces are produced using methods of micro or precision engineering technology.

11. Microreactor in accordance with claims 1 through 10, characterized by the fact that mixers, heat exchangers, dwell spaces, filters, condensers, distillation columns, or extraction columns are provided as integrated function modules.

12. Process for production of a microreactor for conducting chemical reactions in accordance with one of the claims 1 through 11, which has the following steps:

- (d) production of many plates or laminae, the surfaces of which are treated by microtechnology or precision engineering technology such that they have sealing zones and — together with the surfaces of another plate or lamina — horizontal reaction spaces
- (e) stacking of individual plates or laminae in a suitable sequence and orientation in a made-to-fit housing, and
- (f) Compression of the housing cover so that the sealing zones of the individual plates or laminae are compressed in a sealing manner.

13. Construction assembly for making a microreactor for conducting chemical reactions in accordance with one of the claims 1 through 11, which has the following components:

- (d) an assembly of several plates or laminae, the surfaces of which have integrated sealing zones and — together with the surfaces of another plate or lamina — horizontal reaction spaces
- (e) one or more devices in which the individual plates or laminae can be stacked in a made-to-fit housing and arranged in various appropriate sequences, and
- (f) devices for pressing the plates or laminae together so that the sealing zones of individual plates or laminae are compressed together in a sealing manner.

14. Method for conducting chemical reactions, characterized by the fact that one or more chemical reactants in gas form and / or fluid form are mixed together if necessary and brought to reaction in two or more stacked plates or laminae of a microreactor in accordance with claims 1 to 12.

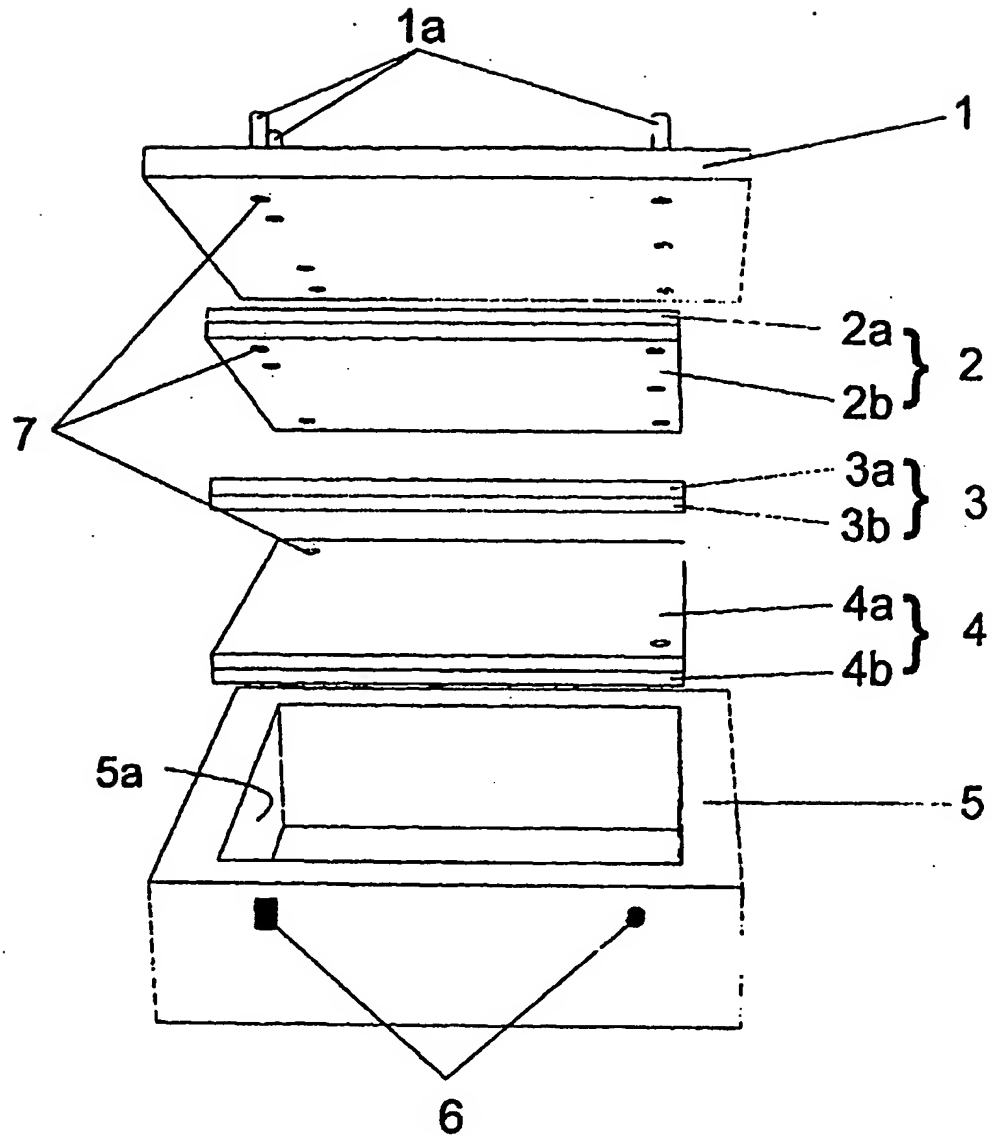


Fig. 1

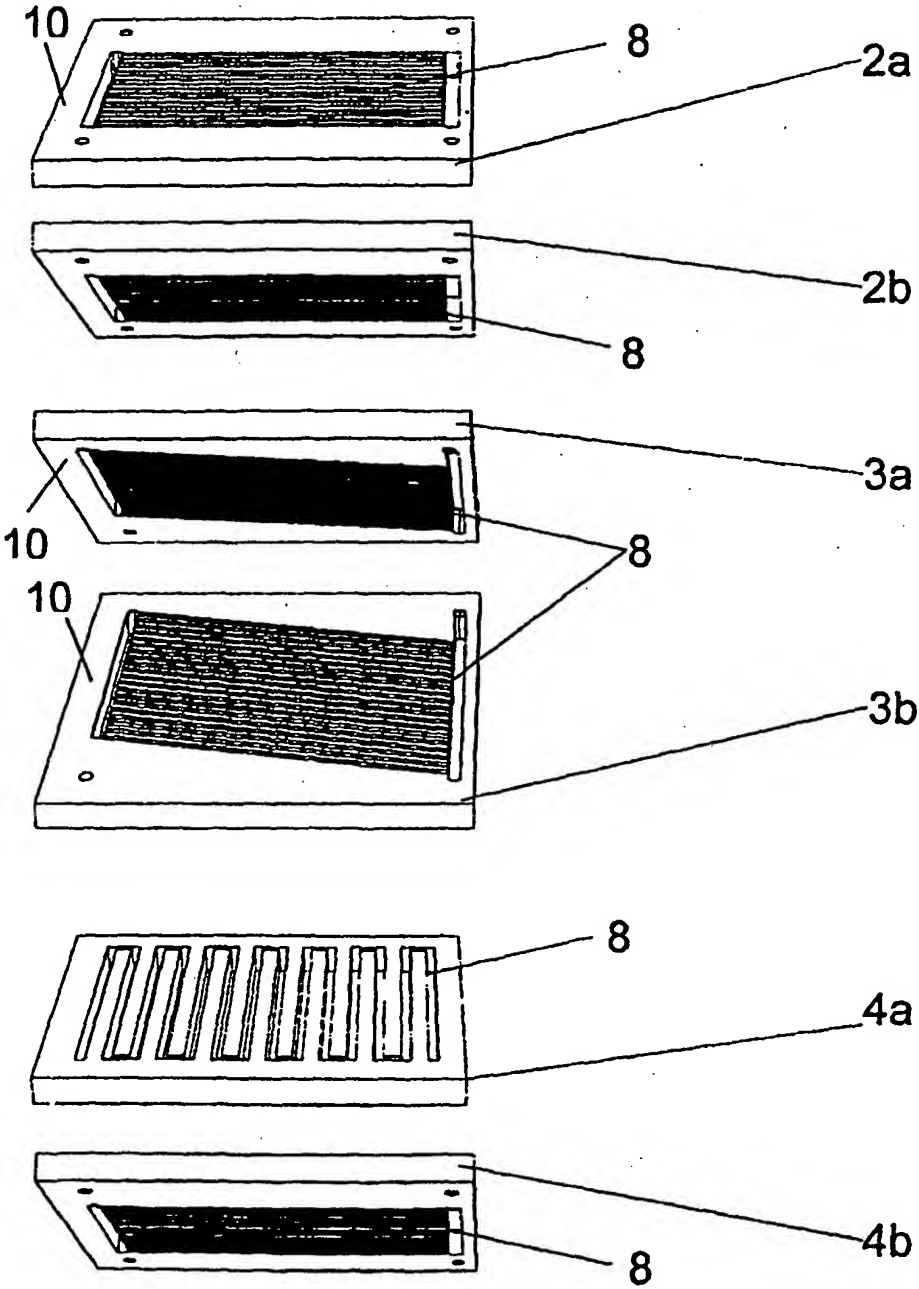


Fig. 2

